

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: Art Unit: 1793  
Peter Gamon Johns  
Application number 10/559,092 Examiner: Sikyin Ip  
Filing Date: 1 June 2004

Title: SILVER TERNARY ALLOY

**DECLARATION PURSUANT TO 37 CFR s 1.132**

1. I, Charles Allenden, have extensive knowledge of and experience with metallurgy, in particular the metallurgy of silver alloys. I obtained a BSc in Metallurgy and Microstructural Engineering from Sheffield Hallam University, in the UK, in 1989. I have extensive knowledge of the production and fabrication of silver alloys following 17 years employment with the UK's largest primary silver manufacturer where I oversaw all technical issues involving alloy manufacture.

In addition I am a qualified quality systems auditor and have acted as a reviewer for the Institute of Mining, Minerals and Materials in the UK for publications involving precious metal casting and thermochemical processes.

2. From my own researches, and from research results that I have studied, I know that changes in silver concentration in a silver alloy can have a significant effect on material properties. The following sections describe experimental results that illustrate this point, in relation to silver alloys containing copper, with about 1.3 wt% germanium and a few ppm B. These show that as the silver concentration is raised from 93% to 94% there is an abrupt decrease in copper elution, and an abrupt increase in thermal processing stability; and that as the silver concentration is raised from 95.5% to 96% there is an abrupt decrease in firestain resistance.

**3. Copper Elution**

Experiments have been carried out using specimens of a range of different silver alloys with silver concentrations between 93.5% and 97.3%, in each case with germanium at about 1.3 wt% and with boron at about 4 ppm, with the remainder being copper. These different alloys were then subjected to a copper elution test based on BS EN 1811:1999, in which the samples are exposed to synthetic sweat solution for 1 week. The elution rate of copper is then quantified by spectrophotometric analysis of the liquid. The results were as follows, in which the figures for the elution rate are given in micrograms of copper/cm<sup>2</sup>/week. Corresponding results are also shown for conventional sterling silver (92.5% Ag/7.5% Cu):

| Silver Concentration | Elution Rate |
|----------------------|--------------|
| 93.5%                | 13.1         |
| 94.1%                | 4.8          |

|          |      |
|----------|------|
| 95.6%    | 4.49 |
| 96.3%    | 4.24 |
| 97.3%    | 0.96 |
| Sterling | 5.84 |

These figures show that the elution rate of copper from these alloys decreases as the silver concentration increases. However the elution rate of copper from these silver alloys is higher at 93.5% Ag (with Cu and Ge) than for 92.5% (sterling) silver. The most dramatic change is between 93.5% and 94.1% Ag (with Cu and Ge), where the elution rate drops from a value more than twice that for sterling silver, to a value less than that for sterling silver.

#### 4. Firestain Resistance

Experiments have been carried out on a range of different silver alloys with silver concentrations between 95.2% and 97.2%, in each case with germanium at about 1.5 wt% and with boron less than 10ppm, with the remainder being copper. These different alloys were then annealed five times in air with a gas/air torch (typical of silversmithing practice when producing a complex item) and then had one end polished to reveal the extent of the copper oxide (firestain) penetration.

| Silver Concentration | Firestain Resistance |
|----------------------|----------------------|
| 95.2%                | Good                 |
| 95.45%               | Good                 |
| 96.0%                | Poor                 |
| 97.2%                | Poor                 |

These results show that between a silver content of 95.45% and 96.0% a silver alloy which contains 1.5% germanium, the balance copper, changes from being highly resistant to copper oxide (firescale) formation when heated in air to having poor firescale resistance. This is a significant change, and takes place abruptly as the composition of the alloy is altered.

I attach a Report entitled "Comparison of Firescale Resistant Properties for High Silver Content Argentium Silver Alloys", giving more detail of this experiment.

#### 5. Improved Thermal Processing Properties

Experiments have been carried out on a range of different silver alloys with silver concentrations between 93.0% and 93.7%, in each case with germanium at about 1.2 wt% and with boron less than 10ppm, with the remainder being copper except for one alloy which contained an addition of 0.5% zinc. These different alloys were then heated to a temperature typical for a brazing process to join two pieces of silver together to fabricate a larger item. (Silversmiths to refer to this process as soldering, but by definition of the American Welding Society et al, brazing is a process which produces coalescence of materials by heating them to a suitable temperature and by using a filler

metal having a liquidus temperature above 840°F (450 °C) and below the solidus temperature of the base materials. The filler material is distributed between the closely fitted surfaces of the joint by capillary attraction. Soldering is the same process, but takes place where the liquidus temperature of the filler metal is below 840°F (450 °C)).

| Silver Concentration   | Thermal Stability |
|------------------------|-------------------|
| 93.0%                  | Poor              |
| 93.5% (with 0.5% zinc) | Good              |
| 93.7%                  | Good              |

These results show that between a silver content of 93.0% and 93.7% a silver alloy which contains 1.2% germanium, the balance copper, changes from having poor thermal stability to good thermal stability. These results also show that a zinc addition can be used to improve thermal stability in addition to the increase in silver content.

I attach a Report entitled "Improving the thermal stability of Argentium sterling silver during thermal processing", giving more detail of this experiment.

#### **6. Restrictions due to Historical Levels of Silver Fineness in Luxury Silver Alloys.**

All silver alloys that are developed to meet hallmarking requirements are entering a competitive market place. For this reason one of the most important constraints on alloy development is cost. To that end the silver content of the alloy is the most important aspect in costing. For this reason alloys are tightly controlled in manufacture to near to the national hallmarking requirements. That is 925 parts silver (minimum) per 1000 for Sterling silver and 958 parts silver (minimum) per 1000 for Britannia grades.

As the greatest cost component in any silver alloy is the value of the silver itself, the minimum silver content required to meet the minimum assay requirements is tightly controlled. For Sterling grades the silver content would be typically controlled at 927 parts per 1000 and for the Britannia grade 960 parts per 1000 in the manufacturing environment, to avoid waste of silver due to too high a silver concentration, whilst ensuring the minimum hallmarking requirements are met.

#### **7. Reduction in Eutectic content by controlling Compositional Limits.**

Thermodynamic assessments (binary phase diagrams for silver-copper, copper-germanium and silver-germanium) show that copper and germanium form the  $\text{Cu}_3\text{Ge}$  phases  $\epsilon$ ,  $\epsilon_1$  and  $\epsilon_2$ . For ease these will be considered as a single stoichiometric phase  $\epsilon$ .

The thermodynamic assessments also make clear that there is a  $\zeta$  phase present which has a hexagonal close packed (hcp) crystal structure (compared to the more typical face centred cubic (fcc) structure typical of alloys which have good formability). This  $\zeta$  phase would form the eutectic. Within the compositional limits of the silver alloys considered

by this patent application the crystal structures vary from fcc to hcp in this critical area of the copper-germanium phase diagram.

Common practice would be to control the rate of cooling to ensure that the phases, and hence crystal structure desired, were precipitated preferentially (for example in steel making to create desired levels of ferrite, pearlite, austenite etc.). This then controls the resultant physical properties of the finished item in terms of formability and hardness.

However this technique of simply adjusting the cooling rate cannot be utilised with this range of silver alloys. This is due to the vast number of different melting procedures in use in the industry, ranging from for example hand held torch melting, and small lost wax investment casting machines for jewellery items, up to continuous casters producing 3000 kg of cast sheet. Although the use of a grain refiner improves the characteristics of the alloy, it does not remove all its deleterious properties.

By controlling the compositional ratio of the copper and germanium to around 3:1 this will promote the formation of the  $\text{Cu}_3\text{Ge}$  phase,  $\epsilon$ . By ensuring that there is a slight excess of copper present above this 3:1 Cu:Ge ratio, the excess copper is present to allow the formation of the silver-rich  $\alpha$  solid-solution of silver and copper, typical of the binary silver-copper alloy. However the optimum level of germanium is 1.2 – 1.5%, so to enable this ratio between copper and germanium to be achieved the silver content of the alloy must be raised above the level for sterling silver (92.5%). By complying with these limitations it is possible to avoid the formation of the eutectic composition and the  $\zeta$  phase with its hcp crystal structure which is well documented to be a poor crystal structure for formability.

This increase in the silver level within the alloy to control crystal structure, rather than controlling the cooling rate of the molten alloy, is a novel solution to the management of the crystal structure in this range of silver alloys, and hence resultant physical properties of the alloy. It is contrary to the conventional best practice within the silver manufacturing industry, where silver content is very tightly controlled to reduce costs.

8. I declare that all of the above statements made of my own knowledge are true and all statements made on information and belief are believed to be true. I understand that wilful false statements and the like are punishable by fine or imprisonment, or both (18 U.S.C. s.1001), and may jeopardise the validity of the application or any patent issuing thereon.

Date: 10th August 2009.

By: 

Charles Allenden

# ARGENTIUM SILVER

## COMPARISON OF FIRESCALE RESISTANT PROPERTIES FOR HIGH SILVER CONTENT ARGENTIUM SILVER ALLOYS

This report demonstrates:

- The firescale resistant properties of Argentium Silver alloys with silver content below 95.5%.
- The loss of firescale resistant properties for Argentium Silver alloys with a silver content including and above 96%.

### ALLOY COMPOSITIONS

#### Composition of alloy A:

|           |   |         |
|-----------|---|---------|
| Silver    | - | 95.2%   |
| Germanium | - | 1.5%    |
| Boron     | - | <10 ppm |
| Copper    | - | Balance |

#### Composition of alloy C:

|           |   |         |
|-----------|---|---------|
| Silver    | - | 96.0%   |
| Germanium | - | 1.55%   |
| Boron     | - | <10 ppm |
| Copper    | - | Balance |

#### Composition of alloy B:

|           |   |         |
|-----------|---|---------|
| Silver    | - | 95.45%  |
| Germanium | - | 1.5%    |
| Boron     | - | <10 ppm |
| Copper    | - | Balance |

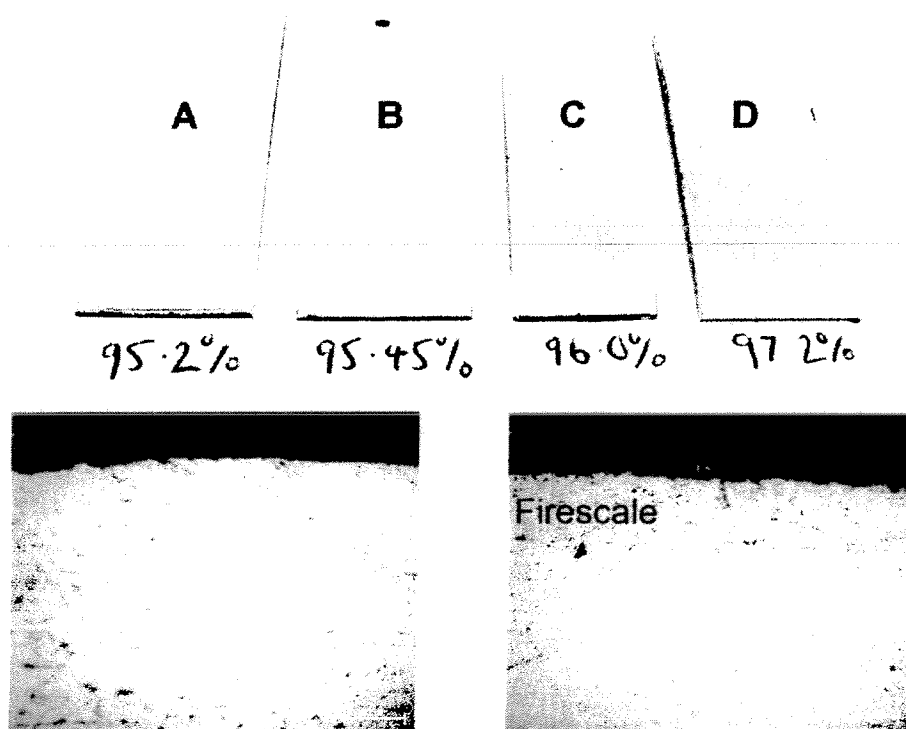
#### Composition of alloy D:

|           |   |         |
|-----------|---|---------|
| Silver    | - | 97.2%   |
| Germanium | - | 1.5%    |
| Boron     | - | <10 ppm |
| Copper    | - | Balance |

### METHOD

Each alloy was annealed 5 times in air with a gas/air blow torch. The samples are then polished hard at one end to reveal the extent of the firescale layer.

### RESULTS:



Left: example shows firescale free surface Right: example shows firescale penetration

# ARGENTIUM SILVER

## IMPROVING THE STABILITY OF ARGENTIUM STERLING SILVER DURING THERMAL PROCESSING

### AIM

The purpose of this test is to demonstrate how:

- Sterling grade alloys containing sufficient germanium (1.2%) to prevent firescale suffer from incipient melting. This gives rise to excessive distortion during normal soldering operations.
- Changes in alloying composition can reduce the incipient melting and resolve the 'sagging' problem.

### **Alloy 1 (Argentium Sterling Silver produced by Stern-Leach):**

|           |   |         |
|-----------|---|---------|
| Silver    | - | 93.0%   |
| Germanium | - | 1.2%    |
| Copper    | - | balance |
| Boron     | - | <10ppm  |

### **Alloy 2:**

|           |   |         |
|-----------|---|---------|
| Silver    | - | 93.5    |
| Germanium | - | 1.2%    |
| Zinc      | - | 0.5%    |
| Copper    | - | balance |
| Boron     | - | <10ppm  |

### **Alloy 3:**

|           |   |         |
|-----------|---|---------|
| Silver    | - | 93.7    |
| Germanium | - | 1.2%    |
| Copper    | - | balance |
| Boron     | - | <10ppm  |

### METHOD

Strips of three different germanium containing silver alloy compositions were cut to the same size. The thickness of each alloy strip measured 0.9mm.

Each sample was placed on top of steel cotter pins on a heatproof tile (as shown in the images below).

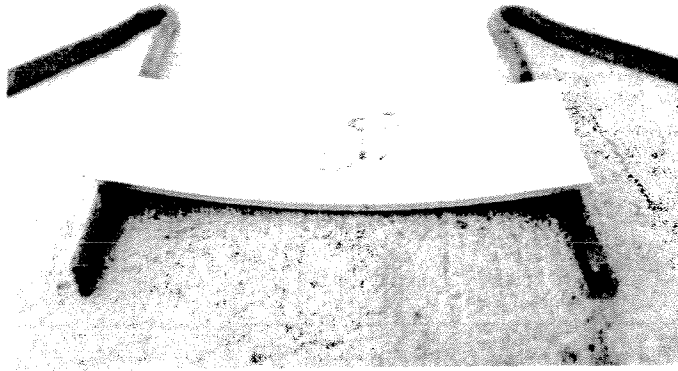
The samples were then heated with a natural gas/compressed air torch to a temperature that would melt a standard 'hard' solder (melting range of 745°C to 778°C).

Flux supplied by Johnson Matthey - No.25.

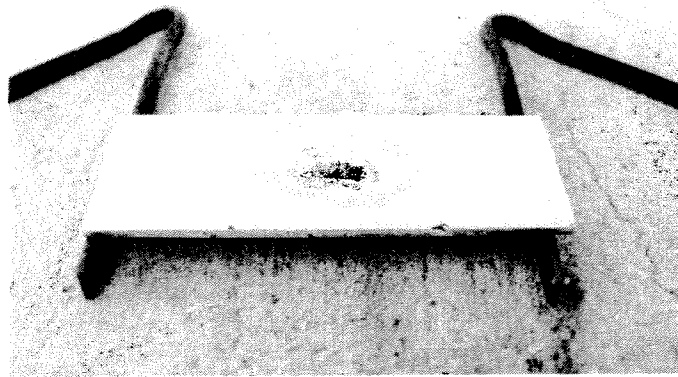
Report: "REDUCING OR PREVENTING THE FORMATION OF COPPER/GERMANIUM EUTECTIC DURING THERMAL PROCESSING OF ARGENTIUM STERLING SILVER" Clare Felgate: 27-July-09

# ARGENTIUM SILVER

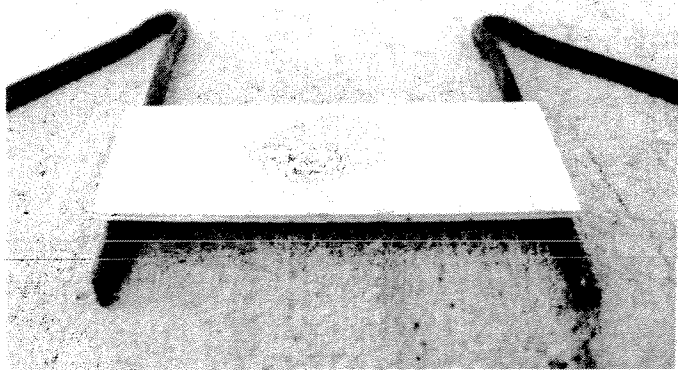
## RESULTS



Alloy No. 1



Alloy No. 2



Alloy No. 3

## OBSERVATIONS

- Alloy No. 1 demonstrates considerable thermal distortion (sagging) when heated to the melting temperature of 'hard' solder.
- Alloys No. 2 and No. 3 have not 'sagged' when heated to the melting temperature of 'hard' solder.

Report: "REDUCING OR PREVENTING THE FORMATION OF COPPER/GERMANIUM EUTECTIC DURING THERMAL PROCESSING OF ARGENTIUM STERLING SILVER" Clare Felgate: 27-July-09

# ARGENTIUM SILVER

## CONCLUSIONS

For Argentium Sterling Silver alloys containing a sufficient level of germanium to prevent firescale (1.2%), this test has shown that by slightly increasing the silver level above that of standard Argentium Sterling Silver (93%), it is possible to reduce or prevent the formation of copper/germanium eutectic during heating processes. This provides the higher silver content Argentium Sterling Silver alloys with a much greater inherent stability when heated to annealing and soldering temperatures.